

Electronic Structures of Polyatomic Molecules and Valence VI. On the Method of Molecular Orbitals

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In concluding, we feel that the experimental evidence is not in agreement with the theories of Van Vleck and Schlapp and Penney and that their basic model will have to be changed to conform with the following experimental evidence from chrome alum. The energy levels appear in groups of closely spaced levels, the lowest *group* belonging to the quartet system.

These levels split in a magnetic field and possess a *g* factor very close to 2. Any interaction between the levels, if it exists, must be very small, of the order of magnitude of 10 percent or less of the splitting. In addition, these levels cannot show a second-order Zeeman effect of more than 5 percent of the normal Zeeman splitting in fields of 25,000 gauss.

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Electronic Structures of Polyatomic Molecules and Valence

VI. On the Method of Molecular Orbitals

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The use of the method of nonlocalized molecular orbitals in building up a *conceptual scheme* or qualitative theoretical framework into which empirical data (chemical and spectroscopic) can be fitted, is emphasized. This should be distinguished from the use of the method, often with rough "LCAO" approximations (linear combinations of atomic orbitals), in semiquantitative calculations.

IN earlier papers of the present series and elsewhere¹ an attempt is made to describe and interpret electronic structures of molecules in terms of electron configurations composed, so far as reasonably possible, of molecular orbitals. Since the object of this work seems not to have been made entirely clear, it seems desirable to restate it briefly.

The whole matter turns about the meaning and use of the idea of electron configurations. Ever since Bohr succeeded in explaining the main features of atomic structures and spectra and of the periodic system, electron configurations have been in constant use for describing atomic structures approximately. Each electron is assigned to a definite orbit (or orbital, in the quantum mechanics), having a fairly definite energy or term value, at least for an atom in a

definite state of ionization. It must be agreed, to be sure, that this term value varies somewhat depending on the state of the atom-as-a-whole, e.g., $3p$ has somewhat different term values in $\cdots 3s3p$, 3P and $\cdots 3s3p$, 1P .

The quantum mechanics, of course, shows that the concept of an electron configuration is in final analysis incompatible with an exact correct description of the electronic structure of an atom. Nevertheless it shows, particularly when Hartree's idea of the self-consistent field is introduced, that one can still in ordinary cases use a unique electron configuration as a basis for a simple and relatively good approximation. (Wave function of atom = antisymmetrical linear combination of permutations of a definite electron configuration assignment.)

With molecules, matters become more complicated. Because of the less simple force field, the possibility of specifying a unique electron configuration tends more easily to be lost. In other words, the inexactness of the electron configuration idea is sufficiently great here to admit the possibility of two or more alternative electron configurations each of which may form the basis for a fairly good approximation to the complete wave function. In such a situation, as

¹ This series: R. S. Mulliken, *Phys. Rev.* **40**, 55; **41**, 49, 751 (1932); **43**, 279 (1933); I, II, III, IV; *J. Chem. Phys.* **1**, 492 (1933); V. Also R. S. Mulliken, *Chem. Rev.* **9**, 347 (1931); *Phys. Rev.* **43**, 765 (1933); **47**, 413 (1935). Also J. E. Lennard-Jones, *Trans. Faraday Soc.* **30**, 70 (1934); in Table III and the text of this paper, the designations T_1 and T_2 have been interchanged as compared with IV of this series, evidently due to a misunderstanding caused by excess of brevity in the writer's discussion of electric moment components in IV. Also papers of Hund, Herzberg, Hückel and others.

Slater has pointed out,² we are forced to adopt views of molecular electronic structures which are more or less intermediate between those suggested by the alternative configurations. In this way we get fairly definite although often complicated pictures of molecular structures. Of course, we might abandon altogether the attempt to use electron configuration ideology; but the time seems not yet ripe for this. In fact, the idea of electron configurations will probably always be valuable as a conceptual aid and in classification.

Methods of assigning molecular electron configurations may be divided into two types. In one of these atomic orbitals are used exclusively; in the other, molecular orbitals of some sort are used for shared electrons. The first method follows the ideology of chemistry and treats every molecule, so far as possible, as composed of definite atoms or ions. The electron configuration is then the sum of the configurations of these atoms or ions, e.g., the normal state of Li_2 may be represented as

$$1s^2 2s \cdot 2s 1s^2, {}^1\Sigma^+_{g_0}. \quad (1)$$

So far as homopolar binding is concerned, this method, which grew out of the work of Heitler and London on H_2 , was developed by Pauling and Slater. It has had notable success as a qualitative conceptual scheme for interpreting and explaining empirical rules of valence and in semiquantitative, mostly semiempirical calculations of energies of formation and other properties of molecular electronic states, particularly the normal states.

Departing from chemical ideology, the second method treats each molecule, so far as possible, as a unit (cf. I and II of this series¹). This method was introduced by Hund for diatomic molecules, and was developed by Hund, the writer, and others. In its pure form, the method goes too far, as was pointed out by Lennard-Jones: it is best to use molecular orbitals only for shared electrons and atomic orbitals for the others.³ Even then, the type of orbitals to be used may often be chosen in various ways: one may use exclusively two-center ("localized") orbitals even for poly-

atomic molecules (Hund), or one may use many-center ("nonlocalized") orbitals for the latter (*present method*). These possibilities of course reduce to one in the case of diatomic molecules. As an example, the normal state of Li_2 appears as

$$1s^2(\sigma_g 2s)^2 1s^2, {}^1\Sigma^+_{g_0},$$

or

$$1s^2(2s + 2s, \sigma_g)^2 1s^2, {}^1\Sigma^+_{g_0}. \quad (2)$$

where $\sigma_g 2s$ and $(2s + 2s, \sigma_g)$ are two types of shorthand for representing the bonding molecular orbital.⁴

It is the writer's belief that, of the various possible methods, the present one may be the best adapted to the construction of an exploratory *conceptual scheme* within whose framework may be fitted both chemical knowledge and data on electron levels from molecular spectra. A procedure adapted to a broad survey and interpretation of observed relations is here aimed at, rather than (at first) one for quantitative calculation, which logically would follow later. Given an observed molecule or ion of known shape and size, what is its electronic structure in terms of an electron configuration using, in general, non-localized orbitals for shared electrons? What is the relation of this structure to the molecule's spectrum, to its ions, and to the structures of other similar and dissimilar molecules? This procedure has already yielded good results for diatomic molecules,⁴ and it is now a question of extending it to polyatomic molecules.¹ To a considerable extent the present method and objective are very analogous to those used by Bohr in developing the theory of atomic structure.⁵

Various limitations and qualifications must of course be recognized. In particular the usefulness of the present method is confined to cases where internuclear distances (r) are fairly small, as in stable molecules. In other cases, or in studying processes of dissociation, the present method must be supplemented by comparison with that using atomic orbitals alone. Even for stable molecules, comparisons should always be made with the latter method, if maximum insight is to be secured.²

⁴ Cf., e.g., R. S. Mulliken, *Rev. Mod. Phys.* **4**, 1 (1932); see sections A3, A8, D1 in regard to notation; for energy levels of H_2 , cf. p. 46. Cf. also *Phys. Rev.* **46**, 549 (1934), on new notation.

⁵ This was noted in the early papers on diatomic molecules: R. S. Mulliken, *Phys. Rev.* **32**, 186 (1928); F. Hund, *Zeits. f. Physik* **51**, 579 (1928); cf. also G. Herzberg, *Zeits. f. Physik* **57**, 601 (1929); J. E. Lennard-Jones.³

² J. C. Slater, *Phys. Rev.* **41**, 255 (1932).

³ J. E. Lennard-Jones, *Trans. Faraday Soc.* **25**, 668 (1929). The method could thus now more accurately be called the "method of atomic and molecular orbitals," but it is the use of *molecular* orbitals which constitutes the distinguishing and vital feature of the method.

As a simple illustration of the difference between the use of atomic and of molecular orbitals, we may consider the three lowest electron levels of the H_2 molecule, *all* taken for an internuclear separation 0.74×10^{-8} cm equal to the equilibrium separation (r_e) of the normal state of H_2 . In terms of the probable best simple electron configuration in each case, these three states appear, by using atomic orbitals, as

$$1s \cdot 1s, {}^1\Sigma^+_g; 1s \cdot 1s, {}^3\Sigma^+_u; 1s^2, {}^1\Sigma^+_u, \quad (3)$$

the third configuration corresponding to $H-H^+$ or H^+H^- . Using molecular orbitals, we have

$$(1\sigma_g)^2, {}^1\Sigma^+_g; 1\sigma_g 2p\sigma_u, {}^3\Sigma^+_u; 1\sigma_g 2p\sigma_u, {}^1\Sigma^+_u. \quad (4)$$

Here " $1\sigma_g$ " is often written as $(1s+1s, \sigma_g)$ or $\sigma_g 1s$. The molecular ionization potential, for a process without change of the internuclear distance, has approximately the respective values 16.3, 6.6 and 3.9 volts for the above states ${}^1\Sigma^+_g$, ${}^3\Sigma^+_u$, and ${}^1\Sigma^+_u$.

From the atomic orbital viewpoint (3), the values 16.3 and 6.6 must be interpreted as 1s term values for the H atom in two states of combination, and 4 volts as the term value of 1s in $1s^2$ of H^- when combined with H^+ . The 1s term value in uncombined H is 13.53 volts, in H^- it is 0.715 volt. The great divergence between the term values 16.3 and 6.6 is an indication of the poorness of the atomic orbital approximation in this case, since a good electron configuration should yield only moderate variations in term value when the state of coupling of the removed electron is altered. If we use the molecular orbital standpoint (4), we find the term value 16.3 volts for $1\sigma_g$ from ${}^1\Sigma^+_g$, and the values 6.6 and 3.9 volts for $2p\sigma_u$ from ${}^3\Sigma^+_u$ and ${}^1\Sigma^+_u$, respectively. It will be seen that according to the *criterion of constancy* of the term values of any orbital, the molecular orbital configurations represent (for small r values) the better approximation in this case.

Recent quantum-mechanical calculations of James and Coolidge⁶ on H_2 and Li_2 suggest that the use of carefully constructed molecular orbitals for shared electrons may often give better

quantitative results even in calculating dissociation energies and other molecular constants than do methods using only atomic orbitals. Previously it had been argued that the reverse is the case.⁷ This argument and its conclusion, however, really never referred to the use of molecular orbitals as such, but only to a particular and decidedly rough type of approximation in which each molecular orbital is expressed as a very simple linear combination of atomic orbitals ("*LCAO molecular orbitals*," let us call them). [Example: the LCAO approximation for $\sigma_g 2s$ of Li_2 is $a(2s_A + 2s_B)$, where A, B refer to the two Li atoms.]⁸

A similar statement applies in part to the criticism⁹ that the use of molecular orbitals gives over-ionic wave functions (e.g., too much H^+H^- character for H_2). When a molecular orbital is occupied by a pair of electrons, overioneness makes the latter spend too much of their time *together behind* the nuclei which are connected by the orbital. It is probable that the overioneness resulting from the use of LCAO approximate molecular orbitals is in general much reduced when better approximations are used for the orbitals. This is for example strikingly brought out by the work of James on Li_2 , which shows that when a better approximation is used for the bonding molecular orbital, the fraction of time spent by an electron behind the Li atoms as compared with that spent between them is much less than for an LCAO approximation orbital.

While the LCAO type of approximation is

⁷ Cf., e.g., G. W. Wheland, J. Chem. Phys. 2, 474 (1934), who, however, favors the use of molecular orbitals in a qualitative way; and cf. some of the references given by him.

⁸ In early papers,⁶ Hund and the writer used for diatomic molecular orbitals a notation ($2p\sigma, 3s\sigma, 3d\pi$, etc.) corresponding to a correlation with the united atom. Lennard-Jones, on the other hand,⁹ emphasized a point of view and introduced a notation ($2p\sigma, 2p\sigma'$, etc., later replaced by Hund or the writer with $\sigma_g 2p, \sigma_u 2p$ or $\sigma 2p, \sigma' 2p$, later also the more explicit forms $(\sigma + \sigma, \sigma_g)$, $(\sigma - \sigma, \sigma_u)$) corresponding to the LCAO approximation. Similar notations of both types have been introduced¹ for polyatomic cases. It has never been intended that any of the various notations^{4, 1} should be interpreted too literally, since the real molecular orbitals are not in general closely approximated by either united-atom or LCAO approximations. If used cautiously with this understanding, however, the various notations can be more helpfully suggestive than misleading. In most cases, the LCAO notations are decidedly the more appropriate,³ but in many cases, especially for excited orbitals, the united-atom or related notations are the better.

⁹ Cf. especially J. H. Van Vleck, J. Chem. Phys. 1, 177 (1933).

⁶ H. M. James and A. S. Coolidge, J. Chem. Phys. 1, 825 (1933); H. M. James, J. Chem. Phys. 2, 794 (1934); 3, 9 (1935). The authors for the most part did not use pure molecular orbital configurations, but their work nevertheless indicates that these would give rather good approximations.

very simple and convenient as a qualitative guide, it is in no way an essential part of the present method. Especially is it not essential to the qualitative conceptual scheme of the latter.⁵ Nevertheless, it was through the use of LCAO forms that a clear understanding of the bonding properties of molecular orbitals was first obtained. This was brought to the front especially by a paper of Lennard-Jones,³ led up to by work of Herzberg.⁵ In subsequent work, LCAO forms have been found reliable guides to the bonding or antibonding properties of orbitals.

The arguments as to the poor quantitative results obtained with molecular orbitals were based also on the idea that detailed interactions between electrons (analogous to those which give rise to atomic levels with different L and S values in atoms) cannot feasibly be taken care of in this method.⁹ Although it is true that the inclusion of such interactions would make quantitative calculations very complicated if one should attempt a completely theoretical calculation from the beginning, their qualitative inclusion has always formed a vital part of the method of molecular orbitals used as a *conceptual scheme* for the interpretation of empirical data on electronic states of molecules. In this case, the term values of molecular orbitals are obtained largely empirically (from band spectra or ionization potential data), and it then remains as a theoretical problem only to estimate the detailed interactions between electrons. For instance, it is precisely because of the inclusion of such interactions that the present method was able to offer the first, and a very simple and satisfactory, qualitative explanation of the paramagnetism of oxygen gas. The theory of the electronic states, including the qualitative energy order, for specified electron configurations of molecular orbitals in diatomic molecules is rather well developed,³ comparing favorably with early stages in the theory of the energy states of electron configurations of atomic orbitals in atoms.

In the development of the theory of atomic structure and spectra, the concepts of orbits and later orbitals were long used freely in correlating empirical data without any necessity of being able always to obtain from pure theory the exact forms of the "real" or "best" (Hartree self-consistent field type) orbits or orbitals, or the

energy order of the various states whose existence was predicted on the basis of combinations of quantum vectors. These various forms and interactions were, in fact, most easily semi-quantitatively determined by fitting the empirical data into the qualitative theoretical framework.

In developing a similar qualitative theory for molecules, the use of LCAO forms for molecular orbitals, although not fundamental, is nevertheless convenient, as has been mentioned, since these are capable of correctly representing symmetry properties and other main qualitative features of the "real" or "best" orbitals. It is, however, these real or perfect, even if not exactly known, orbitals which are used conceptually in the interpretation of empirical data.

In the case of diatomic molecules, more or less nearly perfect "real" orbitals have long been known for the one-electron molecule H_2^+ ; here elliptical coordinates are appropriate. It has long been realized that fairly good approximations might also be obtainable in terms of elliptic coordinates for the orbitals of many-electron diatomic molecules. It remained, however, for James and Coolidge⁶ (cf. especially the last paper of James) to extend this method so as to get fairly good approximations. James makes use of power series with coefficients determined so as to minimize the energy. While the use of series in ordinary elliptic coordinates has thus given good results, one hopes that the use of other or more general types of coordinates may give even better molecular orbitals.

It appears reasonable to expect that, as time goes on, analogous methods will be developed for polyatomic molecules, using expansions involving coordinates adapted to the symmetry of the molecule or of the particular orbital. For example, the nonlocalized molecular orbitals used for CH_4 in the present method¹ could probably best be developed as series using spherical polar coordinates.

In connection with any electron configuration method, it must of course always be remembered that the orbitals used have a meaning only in relation to the electron configuration type of approximation, and only in relation to the particular way chosen for assigning an electron configuration.